ROLE OF CO$_2$ IN THE INITIATION OF CHAIN GROWTH DURING THE FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Data are presented to show that alcohols produce hydrocarbons during the Fischer-Tropsch Synthesis (FTS) that are not consistent with a simple initiation mechanism. CO$_2$ is produced directly from the alcohol, and not by the reverse of the carbonylation reaction. CO$_2$ also initiates chain growth in the FTS, and the initiation intermediate is presumed to be the same intermediate as in the water-gas-shift reaction.

INTRODUCTION

The Fischer-Tropsch Synthesis involves the production of many hydrocarbon and oxygenate products from CO and H$_2$. This makes the analysis of the products very difficult and adds much complexity to the interpretation of the data to develop a consistent mechanism for the reaction. In an effort to obtain data to aid in understanding this complex system, isotopic tracer studies have been utilized. One approach has employed ^{14}C-labeled intermediates (1-6). The early results from the use of ^{14}C-labeled intermediates led to the proposal of an oxygen containing structure that is considered to be responsible for the initiation of the growing chain on the surface of iron catalysts (1-3). With the advent of surface analytical instrumentation, the presence of carbon, but not a significant amount of oxygen on the catalyst surface led workers to question the role of the oxygenated intermediate, and revived the carbide mechanism. However, this latter carbide mechanism differed from that of the one advanced by Fischer and Tropsch (7), where the synthesis was postulated to occur by utilizing the bulk carbide as an intermediate, since the carbide is now believed to be restricted to a surface metal carbide structure (8).

EXPERIMENTAL

The catalyst utilized for all but one of the experiments described below was a C-73 fused iron catalyst manufactured by the United Catalyst, Inc. Prior to use the catalyst was reduced at 400°C in flowing hydrogen and passivated after decreasing the temperature of the catalyst to room temperature. The passivated catalyst was slurried in octacosane in a one liter continuously stirred tank reactor (CSTR) and again reduced at 262°C for three days. The reaction was conducted using a CO/H$_2$ ratio of 1, 262°C, 8 atm. total pressure and a flow rate of synthesis gas to provide 60% conversion of CO. The ^{14}C-tracer compound was added, using a piston pump or as a CO$_2$/CO gas mixture, so that the carbon added in the tracer was 3 or less atomic % of the total carbon added to the CSTR. Liquid products were collected and analyzed for radioactivity as detailed in an earlier report (9).

Experiments with the [14]CO$_2$ were conducted by adding the labeled-gas to the synthesis gas prior to entering a 1-liter mixing vessel. The catalyst utilized in this synthesis was a proto-type catalyst containing 0.03% K, 12% CuO and the remainder Fe$_2$O$_3$. The experimental conditions were otherwise similar to those reported for the C-73 catalyst.

RESULTS

The results for the radioactivity in liquid alkane fractions show that the normal primary alcohol is incorporated to a much greater extent that the corresponding alpha olefin (Figure 1). This result, as did earlier data, suggests that the oxygen-containing compound is a potential chain initiator.

One of the puzzling aspects of the tracer studies was the observation that the radioactivity/mole of alkane decreased approximately as the logarithm of the with carbon number. It was postulated that this was a result of the FTS involving two surface chains.

Furthermore, one chain produced alkanes, alkenes and oxygenates and was initiated by the added alcohol or alkene while the other chain was not initiated by the alcohol and produced only alkanes. These two chains could not have a common intermediate and would therefore occur on different catalytic sites (10).

Another puzzling aspect of the results obtained during the addition of the ^{14}C-labeled alcohol is the production of CO_2 that contains more ^{14}C/mole than the CO. It is generally believed that the CO_2 that is formed during the FTS with an iron catalyst is formed by the water-gas-shift reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2 .$$
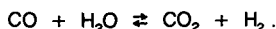
If the primary alcohol formed CO through the reverse carbonylation reaction,

$$RCH=CH_2 + CO + H_2 \rightleftarrows RCH_2CH_2OH,$$
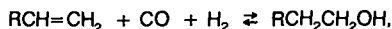
and this CO then underwent the water-gas-shift reaction, the CO_2 would have the same radioactivity/mole as the CO. However, when 1-^{14}C-1-pentanol was added to the synthesis gas the radioactivity/mole of the CO_2 was much greater than that of the CO (Figure 2). This means that the CO_2 could not have been formed by decarbonylation followed by the water-gas-shift reaction. In order to ensure that the results with 1-^{14}C-1-pentanol were reliable, 2-^{14}C-1-hexanol was synthesized and added to the synthesis gas under reaction conditions that were identical to those utilized with 1-^{14}C-1-pentanol. As can be seen from the data in Figure 2, the radioactivity of both CO and CO_2 are below the detection limit while that of pentane is high compared to that of 1-pentene. The radioactivities/mole of the C_3 and C_4 hydrocarbons are below the detection limit. The results in Figure 2 clearly show that the added alcohol has undergone conversion to produce CO_2 that is derived from the carbonyl carbon and that the alkyl group remaining has been converted directly to the alkane rather than to the 1-alkene which is then hydrogenated to the alkane.

The data in Figure 2 are consistent with a mechanism in which the adsorbed alcohol reacts with a surface oxygen; thus, it appears that the reaction can be adequately described by the following mechanism:
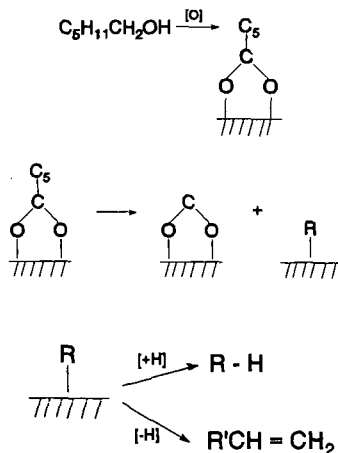
Additional data to support the above mechanism has now been obtained by adding [14]CO_2 to the synthesis gas. If the FTS chains are initiated by species derived only from CO then the hydrocarbon products produced from the experiment with [14]CO_2 could not have a radioactivity/mole that was greater than that of CO. The [14]CO_2 was added so that it contained only 0.3% of the carbon that was added; thus, the composition of the gases in the CSTR was not altered significantly by the added [14]CO_2. The radioactivity/mole of the CO, CO_2, CH_4, and C_2H_6 are given in Table 1.

If the methane had been formed only from CO then the radioactivity/mole of methane and ethane could not have exceeded that of the CO since the experiment was conducted in a CSTR where all of the catalyst particles are exposed to the same gas composition. The

methane has an activity that approaches that of the added CO_2, rather than that of the CO. This requires the formation of methane to be initiated from CO_2. The activity of ethane is also close to that of the CO_2 showing that it is the FTS that is initiated to a large extent by an intermediate derived from CO_2, and not just the formation of methane.

Data for the C_1-C_9 hydrocarbons formed during the addition of $^{14}CO_2$ are presented in figure 3. The CPM/mole for the CO and CO_2 in the exit gas are shown by the solid triangles labeled by CO and CO_2, respectively. It is apparent that the CO_2 has a much higher radioactivty than does the CO. The broken line passing through the radioactivity for the CO represents the increase in radioactivity with carbon number of the hydrocarbon products if they were formed only from CO. In this case each hydrocarbon, C_n, would contain the radioactivity of n carbons derived from the CO. It is clear that the radioactivity of each of the products is much higher than could result from synthesis using CO only. The radioactivity of the hydrocarbon products are shown in open circles, resulting from analysis using the gas analyzer, and open squares, resulting from analysis using a Porpack column that permits the analysis of hydrocarbons of higher carbon numbers. For the moment, we concentrate on the radioactivities of the C_3-C_9 products. The solid line representing these data is parallel to the broken line passing through the radioactivity for CO. For the C_3-C_5 hydrocarbons, the radioactiviy measured using the different g.c. instruments show good agreement. Futhermore, the line defined by the C_3-C_9 hydrocarbons extrapolates to a radioactivity of about 0.8×10^3 CPM/mole. The slope of the solid line in figure 3 indicates that chain growth is primarily due to addition of carbon units derived from CO; the similar slopes of the solid and the broken lines are considered to require this conclusion. However, it appears that about 60% of the hydrocarbon chains that lead to C_3-C_9 hydrocarbon products are derived from CO_2. From the higher activity of the C_1 and C_2 hydrocarbons, it appears that even more than 60% of these products are derived from CO_2 initiation. It therefore seems clear that the data in figure 3 require the species that is responsible for the chain initiation be different from the species that is responsible for chain propogation. Futhermore, the species responsible for chain initiation is derived from both CO_2 and CO but the species that is responsible for chain propagation is derived from CO. Thus, it is concluded that the species that is responsible for chain initiation retains some oxygen, and in this respect is similar to the postulates of Emmett and coworkers.

CONCLUSION

It appears that the FTS mechanism with an iron based catalyst involves an oxygenate species that can be derived from both CO and CO_2. The data generated from the above studies involving the addition of CO_2 or alcohol are consistent with a reaction mechanism that involves reactions as shown above for the alcohol. Thus, the intermediate that is involved in the water-gas-shift reaction is postulated to be an initiator for chain growth for the FTS reaction.

ACKNOWLEDGMENT

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Table 1. Radioactivity/mole of Effluent Gas Products

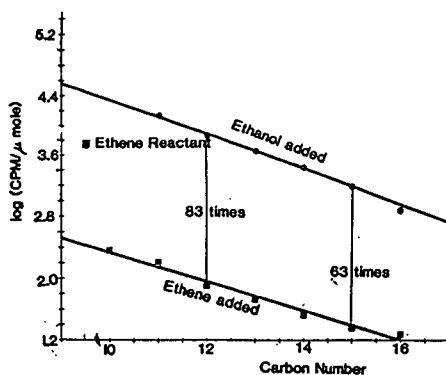| Compound	Radioactivity, Counts/Min./Mole
CO	0.12×10^{-3}
CO_2	1.31×10^{-3}
CH_4	1.12×10^{-3}
C_2H_6	1.28×10^{-3}

Figure 1. The ^{14}C activity in the alkane products formed when 1-pentanol (●) or 2-pentene (■) was added to the syngas feed to a C-73 catalyst (CSTR, 262°C, 8 atm).
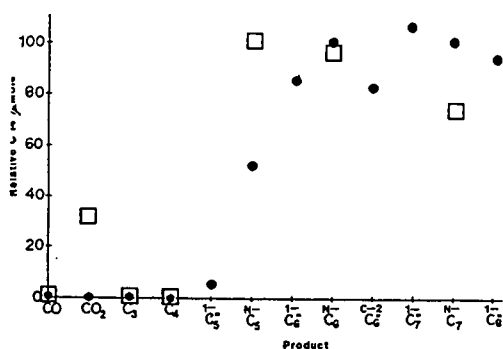

Figure 2. Products (gas phase) from the conversion of a syngas containing either 2-^{14}C-1-hexanol (◆, ●) or 1-^{14}C-1-pentanol (□) with a C-73 catalyst at 262°C and 8 atm (total) in a CSTR.
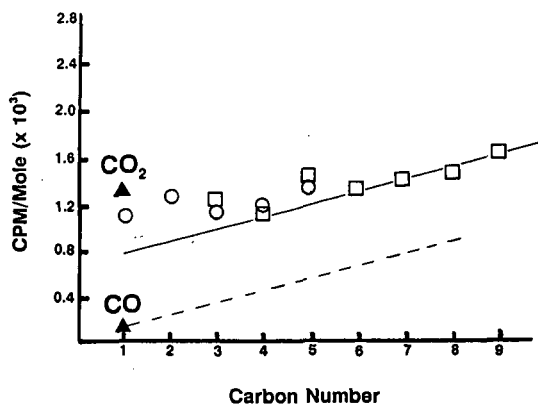
Figure 3. The ^{14}C activity in the alkane products formed when $^{14}CO_2$ is added to the synthesis gas fed to the UCI proto-type iron catalyst (CSTR, 270°C, 8 atm).